(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 242 322**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **87810137.7**

(22) Date of filing: **11.03.87**

(51) Int. Cl.⁴: **C 07 D 231/16**, C 07 D 231/12, C 07 D 231/14, C 07 D 231/22, C 07 D 231/56, C 07 D 409/04, C 07 D 207/34, C 07 D 209/44, C 07 D 235/10, C 07 D 235/06, C 07 D 249/18

(30) Priority: **18.03.86 US 840814**

(43) Date of publication of application: **21.10.87 Bulletin 87/43**

(84) Designated Contracting States: **AT BE CH DE ES FR GB GR IT LI NL**

(71) Applicant: **SANDOZ AG, Lichtstrasse 35, CH-4002 Basel (CH)**
(84) Designated Contracting States: **BE CH ES FR GB GR IT LI NL**

(71) Applicant: **SANDOZ-PATENT-GMBH, Humboldtstrasse 3, D-7850 Lörrach (DE)**
(84) Designated Contracting States: **DE**

(71) Applicant: **SANDOZ-ERFINDUNGEN Verwaltungsgesellschaft m.b.H., Brunner Strasse 59, A-1235 Wien (AT)**
(84) Designated Contracting States: **AT**

(72) Inventor: **Carney, Robert L., 2676 Emerson Street, Palo Alto California 94306 (US)**
Inventor: **Gruber, John M., 565 Willow Road 4, Menlo Park California 94025 (US)**
Inventor: **Lui, Alfred S., 716 Windsor Way, Redwood City California 94062 (US)**

(54) Novel phenylureas.

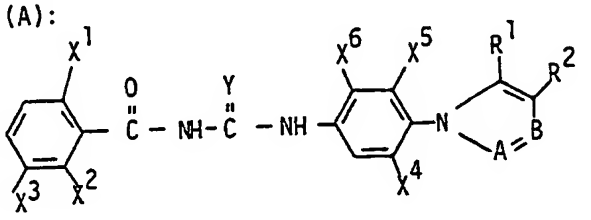
(57) Novel substituted N-(heterocyclic-substituted phenyl)-N'-benzoylureas, processes for producing these compounds, compositions thereof and the use of the compounds for the control of pests.

EP 0 242 322 A2

NOVEL PHENYLUREAS

The present invention relates to novel substituted N-(heterocyclic-substituted phenyl)-N'-benzoylureas, to processes for producing these compounds, to intermediates therefor, to compositions thereof and to the use of the compounds for the control of pests, and in particular for the control of insects and acarids.

More particularly, the compounds of the present invention are represented by the following formula (A):



(A)

wherein, each of X^1, X^2, X^3 and X^5 is independently hydrogen, halogen or C_{1-4}alkyl;

X^4 is hydrogen, halogen, unsubstituted or halogenated C_{1-4}alkyl or COOR;

X^6 is hydrogen, halogen, C_{1-8}alkyl or COOR';

Y is oxygen or sulfur;

A is nitrogen or C-R^4;

B is nitrogen or C-R^3;

each of R^1 and R^4 is independently hydrogen, halogen, halogenated C_{1-8}-alkyl, unsubstituted or halogenated C_{1-8}alkoxy, unsubstituted or halogenated C_{1-8}alkylthio or; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogen atoms or with a CF_3, C_{1-4}alkyl or C_{1-4}alkoxy group and 0 to 3 halogen atoms;

each of R^2 and R^3 is independently hydrogen; halogen; cyano; unsubstituted or halogenated C_{1-8}alkyl; unsubstituted or halogenated C_{1-8}-alkoxy; unsubstituted or halogenated C_{1-8}alkylthio; COOR"; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogenatoms or with a C_{1-4}alkyl, C_{1-4}alkoxy or CF_3 group and 0 to 3 halogen atoms; or either R^1 and R^2 or R^2 or R^3 can together form a bridging group of 4 carbon atoms, saturated or unsaturated, and optionally substituted with 1 to 4 halogen atoms or with a trifluoromethyl group and 0 to 3 halogen atoms;

each of R, R' and R" is hydrogen or C_{1-8}alkyl;

with the proviso that where A is C-R^4 and B is C-R^3, not all of R^1, R^2, R^3 and R^4 may be hydrogen.

In the practice of the present invention, Y is preferably oxygen.

A is preferably nitrogen.

Where A is nitrogen, B is preferably C-R^3.

Where any of the substituents X^1-X^6 and R^1-R^4 is or comprises halogen, such halogen is conveniently selected from bromo, chloro and fluoro.

Where any of X^1-X^6 is C_{1-8}alkyl, it is preferably of one to four carbons and is more preferably of one or two carbons.

Where any of R, R' and R" is C_{1-8}alkyl, it is preferably of one to four carbons and is more preferably of one or two carbons.

The terms halogenated C_{1-8}alkyl, halogenated C_{1-8}alkoxy and halogenated C_{1-8}alkylthio refer to C_{1-8}alkyl, C_{1-8}alkoxy and C_{1-8}alkylthio, respectively, substituted by one to six, preferably one to three halogens; such halogen is preferably chloro or fluoro.

An example of a preferred halogenated C_{1-8}alkyl group is CF_3.

The term aryl as used herein (as such or in the terms aryloxy or arylthio) refers to an aromatic ring system such as naphthyl, phenyl, pyridyl and thienyl; preferably phenyl. Where such aryl is substituted it may bear from 1 to 4, preferably 1 or 2 substituents. Thus aryl, aryloxy and arylthio is preferably unsubstituted or substituted with one methyl, methoxy or CF_3 group and zero or one halogen atoms or with one or two halogen. Particularly preferred substituted aryl significances are halophenyl, dihalophenyl, methylphenyl and trifluoromethylphenyl.

Preferably not more than one of R^1, R^2, R^3 and R^4 is unsubstituted or substituted aryl, aryloxy or arylthio.

X^1 is preferably H or halogen, more preferably chloro or fluoro.

X^2 is preferably hydrogen or halogen; such halogen is preferably fluoro.

X^3 is preferably hydrogen or halogen, more preferably hydrogen.

X^4 conveniently signifies hydrogen, halogen, C_{1-4}alkyl, CF_3 or COOR; it is preferably hydrogen, chloro, bromo, methyl or CF_3.

X^5 is preferably hydrogen, C_{1-4}alkyl or halogen; it is more preferably hydrogen, chloro or methyl.

X^6 is preferably hydrogen or halogen, more preferably H or F.

R^1 conveniently signifies hydrogen, halogen, CF_3, unsubstituted or unsubstituted aryl, C_{1-4}alkoxy or together with R^2 forms a bridging group of 4

carbon atoms. R^1 is preferably hydrogen, bromo, chloro, CF_3, or unsubstituted or substituted phenyl, more preferably hydrogen or chloro.

R^2 conveniently signifies hydrogen, halogen, CF_3, C_{1-4}alkyl, COOR', cyano, unsubstituted or substituted phenyl, or together with either R^1 or R^3 forms a bridging group of 4 carbon atoms. R^2 is preferably hydrogen, halogen, CF_3 or unsubstituted or substituted phenyl. R^2 is more preferably hydrogen, halogen, CF_3 or un-, mono- or disubstituted phenyl, and is particularly H, Cl or Br.

R^3 conveniently signifies hydrogen, halogen, CF_3, C_{1-4}alkyl, unsubstituted or substituted phenyl or together with R^2 forms a bridging group of 4 carbon atoms. R^3 is preferably hydrogen, halogen, CF_3, C_{1-4}alkyl or un-, mono- or disubstituted phenyl, particularly H, Cl, Br, CF_3, 4-chlorophenyl or 4-bromophenyl.

Where R^1 and R^2 together form a bridging group this is preferably of the formula CH=CH-CH=CH; such group is preferably unsubstituted or substituted by 1 or 2 halogen atoms; such halogen is preferably chloro.

Where R^2 and R^3 together form a bridging group this is preferably of the formula $(CH_2)_4$. Such group is preferably unsubstituted or substituted by 1 or 2 halogen atoms; more preferably it is unsubstituted.

Accordingly, in a preferred subgroup of compounds of formula (A)

each of X^1, X^2 and X^3 is independently H or halogen,

X^4 is H, halogen, CH_3 or CF_3,

X^5 is H, halogen or CH_3, X^6 is H or halogen, Y is O, A is N, B is C-R^3,

each of R^1 and R^2 is independently H, halogen or CF_3,

R^3 is H, halogen, C_{1-4}alkyl or CF_3 whereby one of R^1, R^2 and R^3 may also be halophenyl, dihalophenyl, methylphenyl or trifluoromethylphenyl and/or

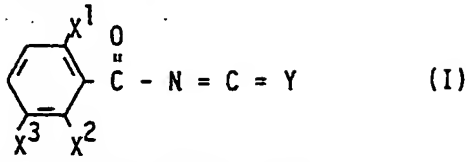
R^1 and R^2 together may form a bridging group of the formula CH=C-CH=CH, which group is unsubstituted or mono- or dihalogenated, or

R^2 and R^3 together form a bridging group of formula $(CH_2)_4$.

The compounds of formula (A) can have one or more asymmetric centers, geometric or positional isomers. The present invention includes each of such isomers or mixtures thereof. In the examples hereinafter such isomers are obtained as mixtures unless otherwise specified.

The compounds of formula (A) are obtained by

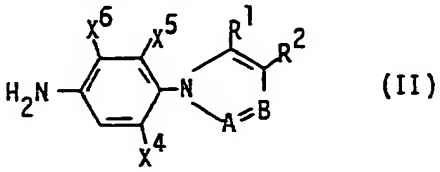
a) reacting a compound of formula (I)



(I)

wherein X^1, X^2, X^3 and Y are as defined above,

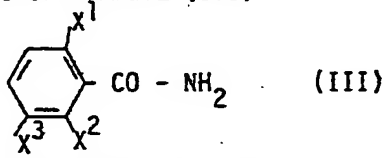
with a compound of formula (II)



(II)

wherein X^4, X^5, X^6, R^1, R^2, A and B are as defined above,

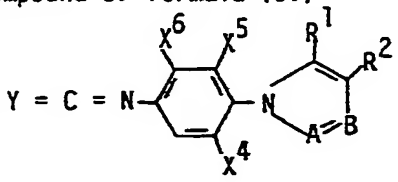
or b) by reacting a benzamide of formula (III)



(III)

wherein X^1, X^2 and X^3 are as defined above,

with a compound of formula (IV)



(IV)

wherein Y, R^1, R^2, X^4, X^5, X^6, A and B are as defined above.

The reaction of compounds of formula I with compounds of formula II (process a) may be effected under the conditions known for the preparation of N-benzoyl-N'-phenylureas from the corresponding isocyanates and anilines.

The reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. methylene chloride or dimethylformamide. A suitable reaction temperature may vary from -10°C to the boiling point of the solvent used, and preferably is about room temperature or moderately above or below room temperature, e.g. between 15 and 25°C.

The reaction of compounds of formula III with compounds of formula IV (process b) may be effected under the conditions known for the preparation of N-benzoyl-N'-phenylureas from the corresponding benzamides and phenylisocyanates. The reaction is conveniently carried out in a solvent which is inert

under the reaction conditions. A suitable reaction temperature is from 0° to 120°C, preferably at the boiling point of the solvent used. The reaction is optionally effected in the presence of an organic base, such as pyridine.

The compounds of formula (A) may be recovered from the reaction mixture in which they are formed by working up by established procedures.

The compounds of formula I can be synthesized by treating the corresponding benzamide with oxalyl chloride or by reacting the corresponding benzoyl chloride with ammonium thiocyanate.

The aniline derivatives of formula II can be prepared by reduction of catalytic hydrogenation of the corresponding nitro compounds.

The isocyanates and isothiocyanates of formula IV can be produced by reaction of the derivatives of formula II with phosgene or thiophosgene.

The starting materials and reagents employed in the processes described herein are either known or, insofar as they are not known, may be produced in a manner analogous to the process described herein or to known processes.

The compounds of formula (A) are chitin inhibitors as indicated by tests with i.a. third instar larvae of Manduca sexta, Musca domestica, Heliothis vireseens and Spodoptera exigua, fourth instar larvae of Aedes aegypti, first instar larvae of Dermestes maculatus. They are accordingly indicated for use as pest controlling agents, particularly for the control of insects, mites and ticks.

In view of their interesting activity, particularly with regard to the level and spectrum of activity, the compounds of formula (A) offer an advantageous alternative for known chitin inhibitors, such as those disclosed in US Pat. Spec. 3 748 356 and UK Pat. Spec. 2 134 518A.

The compounds of formula (A) can be effective control agents for insects of, for example, the orders Lepidoptera, Hemiptera, Homoptera, Coleoptera, Diptera, Orthoptera and Siphonaptera, and other insects, as well as for mites and ticks of the class Acari, including mites of the families Tetranychidae and Tarsonemidae and ticks of the families Argasidae and Ixodidae. The compounds can be applied to the pest or its locus in a pest-controlling amount, usually of the order of 0.001 microgram to 100 microgram per insect, mite or tick, depending on the mode and conditions of application as well as on the pest involved.

Additionally, compounds of formula (A) may possess a repellant and/or anti-feedant action on terrestrial snails and slugs.

In the use of the compounds of formula (A) for combatting pests, a compound of formula (A), or mixtures thereof, can conveniently be employed as pesticidal compositions in association with acceptable diluent(s) for application to the pest or its locus. Such compositions also form part of the present invention.

Suitable formulations contain from 0.01 to 99% by weight of active ingredient, from 0 to 20% of surfactant from 1 to 99.99% of diluent(s). Higher ratios of surfactant to active ingredient are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms of a composition generally contain between 0.01 and 25% by weight of active ingredient. Lower or higher levels of active ingredient can, of course, be present depending on the intended use, the physical properties of the compound and the mode of application. Concentrate forms of a composition intended to be diluted before use generally contain between 2 and 90%, preferably between 5 and 85% by weight of active ingredient.

Useful formulations of the compounds of formula (A) include dusts, granules, suspension concentrates, wettable powders, flowables and the like. They are obtained by conventional manner, e.g. by mixing a compound of formula (A) with the diluent(s) and optionally with other ingredients.

Alternatively, the compounds of formula (A) may be used in micro-encapsulated form.

The compounds of formula (A) can be combined with a cyclodextrin to make a cyclodextrin inclusion complex for application to the pest or its locus.

Agriculturally acceptable additives may be employed in the pesticidal compositions to improve the performance of the active ingredient and to reduce foaming, caking an corrosion, for example.

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulphonate and lauryl sulfate.

"Diluent" as used herein means a liquid or solid agriculturally acceptable material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or diatomaceous earth, for liquid concentrate forms for example a hydrocarbon such as xylene or an alcohol such as isopropanol, and for liquid application forms i.a. water or diesel oil.

The compositions of this invention can also comprise other compounds having bilogical activity, e.g. compounds having similar or complementary pesticidal or insect growth regulating activity or compounds having antidotal, fungicidal, herbicidal or insect attractant activity.

The following examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. RT means room temperature. Parts and percentages are by weight. The symbols *, = and + when used in connection with melting points means "gas", "softens" and "decomposes" respectively. DMF means dimethyl formamide.

COMPOSITION EXAMPLES

Example A:	Dust	
	Compound 14	5.1%
	kaolin	94.9%
Example B:	Flowable	
	Compound 14	48.0%
	dispersant	4.0%
	thickener	0.6%
	antifoam	0.1%
	water	41.3%
	propylene glycol	6.0%
Example C:	Wettable Powder	
	Compound 17	81.0%
	kaolin	14.8%
	dispersant	4.0%
	wetting agent	0.2%

The ingredients are mixed and milled until the mean particle size is about 5 micron.

PREPARATION OF FINAL UREAS

Example 1: N-4-(4-chloro-1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea

2,6-Difluorobenzoyl isocyanate (0.47 g, 2.6 mmol) is added dropwise to a solution of 4-(4-chloro-1-pyrazolyl)aniline (0.50 g, 2.6 mmol) in 8 ml of methylene chloride. The mixture is stirred for 30 min., then diluted with methylene chloride and filtered. The solid is washed with ether and dried to give N-4-(4-chloro-1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea (compound 1 under Table A).

Example 2: N-3,5-dichloro-4-(1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea

To a solution of 3,5-dichloro-4-(1-pyrazolyl)aniline (0.17 g, 0.75 mmol) in 7 ml of methylene chloride and 1 ml of DMF is added 2,6-difluorobenzoyl isocyanate (0.14 g, 0.75 mmol). The resulting miature is stirred for 5 min., then diluted with ethyl acetate, washed with water and with brine, and dried. After the solvent is evaporated off, ether is added to the solid residue, the suspension is filtered and the solid is washed with ether and dried to give N-3,5-dichloro-4-(1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea (compound 2 under Table A).

Example 3

Following generally the procedures of Example 1 or 2, each of the final product ureas under Tables A and B and those listed under column I below is prepared from the corresponding aniline and benzoyl isocyanate or benzoyl isothiocyanate intermediates.

TABLE A

Compounds of formula (A) wherein Y is O, A is N and B is CR_3 :

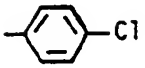
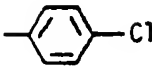
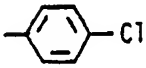
Cpd	X^1	X^2	X^3	X^4	X^5	X^6	R^1	R^2	R^3	m.p. (°C)
1	F	F	H	H	H	H	H	Cl	H	240-242
2	F	F	H	Cl	Cl	H	H	H	H	211-212
3	F	F	H	Cl	Cl	H	H	Cl	H	229-230
4	F	F	H	Cl	Cl	H	H	Br	H	233-235
5	F	F	H	Cl	Cl	H	H	CF_3	CF_3	220-223
6	F	F	H	Cl	Cl	H	H	H	Cl	217-219
7	F	F	H	Cl	Cl	H	H	Br	Br	224-227
8	F	F	H	Cl	Cl	H	H	H		210-212
9	F	F	H	Cl	Cl	H	H		H	246-247
10	F	F	H	Cl	Cl	H	H	H	CF_3	202.5-203.5
11	F	F	H	Cl	Cl	H	H	CF_3	H	222-223
12	F	F	H	Cl	Cl	H	Cl	H	CF_3	206-207
13	F	F	H	Cl	Cl	H	H	H	$C(CH_3)_3$	204-205
14	F	F	H	Cl	Cl	H	H	Cl		206.5-208.5
15	F	F	H	Cl	Cl	H	H	Cl	Cl	231-233
16	F	F	H	Cl	Cl	H	H	Cl	CF_3	222.5-224
17	F	F	H	Cl	Cl	H	Cl	Cl	CF_3	203-204
18	F	F	H	Cl	Cl	H	CF_3	H	CF_3	212.5-214
19	F	F	H	H	H	H	CF_3	H	CF_3	211.5-212
20	F	F	H	H	H	H	Cl	H	CF_3	197-199
21	F	F	H	H	Cl	H	H	Cl	H	230-231

TABLE A (cont.)

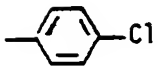
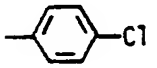
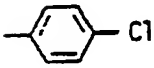
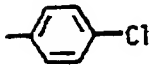
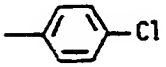
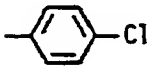
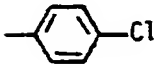
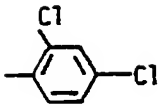
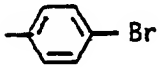
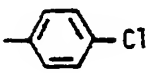
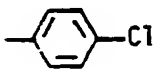
Cpd	X^1	X^2	X^3	X^4	X^5	X^6	R^1	R^2	R^3	m.p. (°C)
535	F	F	H	Cl	H	H	H	Cl		
36	F	F	H	CF_3	H	H	H	Cl		242-244
37	F	F	H	CF_3	H	H	Cl	H	CF_3	192.5-195
10 38	F	F	H	Cl	Cl	H	Cl	Cl	Cl	236-238
39	F	F	H	Cl	Cl	H	H	Br		204-206
40	F	F	H	Cl	Cl	H	Br	Br	Br	249-250
15 41	F	F	H	Cl	Cl	H	CF_3	H	Cl	209-211
42	F	F	H	H	H	F	H	Cl		121.5-122.5
43	F	F	H	Cl	H	F	H	Cl		238-240
20 44	F	F	H	CH_3	H	H	H	Cl		236-238
45	F	F	H	Cl	H	CH_3	H	Cl		208-210
25 46	F	F	H	Cl	Cl	H	H		H	232-234
47	F	F	H	Cl	Cl	H	H		H	253-254
30 48	F	F	H	CH_3	CH_3	H	H	Cl		217-219
49	F	F	H	Cl	Cl	H	OCH_3	Cl		216-217
35 50	F	F	H	Cl	Cl	H	H	$C(O)OCH_2CH_3$	H	213-215

TABLE A (cont.)

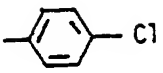
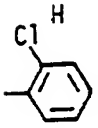
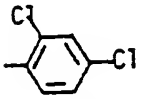
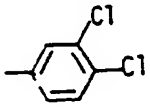
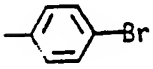
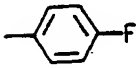
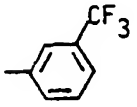
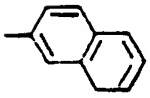
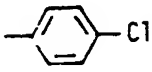
Cpd	X^1	X^2	X^3	X^4	X^5	X^6	R^1	R^2	R^3	m.p. (°C)
51	F	F	H	$C(O)OCH_3$	H	H	H	Cl		210-212
52	F	F	H	Cl	H	H	Cl	H	CF_3	207.5-208.5
53	F	F	H	Cl	H	H	H	Br	H	226-228
54	F	F	H	CF_3	H	H	H	Br	H	206-208
55	F	F	H	Cl	Cl	H	H	H		230-232
56	F	F	H	Cl	Cl	H	H	H		231-232
57	F	F	H	Cl	Cl	H	H	H		224-225
58	F	F	H	Cl	Cl	H	H	H		224-225
59	F	F	H	Cl	Cl	H	H	H		222-224
60	F	F	H	Cl	Cl	H	H	H		199-200
61	F	F	H	Cl	Cl	H	H	H		226-228
62	F	F	H	Cl	Cl	H	H	H		228-229
63	F	F	H	Cl	Cl	H	H	CN	H	246-248
64	F	H	H	Cl	Cl	H	Cl	Cl	CF_3	193-194.5
65	F	H	H	Cl	Cl	H	H	Cl		198-200

TABLE A (cont.)

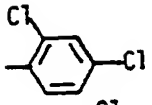
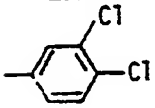
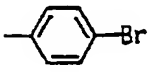
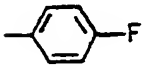
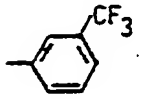
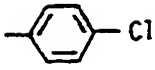
Cpd	X^1	X^2	X^3	X^4	X^5	X^6	R^1	R^2	R^2	m.p. (°C)
66	F	H	H	Cl	H	H	Cl	H	CF_3	202-203
67	F	H	H	Cl	H	H	H	Br	H	213-215
68	F	H	H	CF_3	H	H	H	Br	H	170-172
69	F	H	H	Cl	Cl	H	H	H		215-216
70	F	H	H	Cl	Cl	H	H	H		234-236
71	F	H	H	Cl	Cl	H	H	H		218-219
72	F	H	H	Cl	Cl	H	H	H		199-201
73	F	H	H	Cl	Cl	H	H	H		202-204
74	CH_3	H	H	Cl	Cl	H	Cl	Cl	CF_3	211-212.5
75	CH_3	H	H	Cl	Cl	H	H	Cl		243-245
76	Cl	H	F	Cl	Cl	H	Cl	Cl	CF_3	211-212.5
77	Cl	F	H	Cl	Cl	H	Cl	Cl	CF_3	220.5-222
78	Cl	Cl	H	Cl	Cl	H	Cl	Cl	CF_3	231.5-232.5
79	Cl	H	H	H	H	H	H	Cl	H	
80	Cl	H	H	Cl	Cl	H	H	H	H	200-202
81	Cl	H	H	Cl	Cl	H	H	Cl	H	236-238
82	Cl	H	H	Cl	Cl	H	H	Br	H	234-236
83	Cl	H	H	Cl	Cl	H	H	CF_3	CF_3	195-196
84	Cl	H	H	Cl	Cl	H	H	H	Cl	202-203
85	Cl	H	H	Cl	Cl	H	H	Br	Br	208-210

TABLE A (cont.)

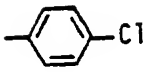
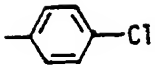
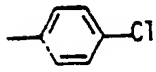
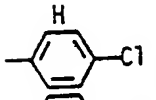
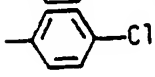
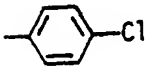
Cpd	X^1	X^2	X^3	X^4	X^5	X^6	R^1	R^2	R^3	m.p. (°C)
86	Cl	H	H	Cl	Cl	H	H	H		201.5-203
87	Cl	H	H	Cl	Cl	H	H		H	227-230
88	Cl	H	H	Cl	Cl	H	H	H	CF_3	
89	Cl	H	H	Cl	Cl	H	H	CF_3	H	207-208
90	Cl	H	H	Cl	Cl	H	Cl	H	CF_3	209-210
91	Cl	H	H	Cl	Cl	H	H	H	$C(CH_3)_3$	200-201
92	Cl	H	H	Cl	Cl	H	H	Cl		229-231.5
93	Cl	H	H	Cl	Cl	H	H	Cl	Cl	220-227
94	Cl	H	H	Cl	Cl	H	H	Cl	CF_3	202-203
95	Cl	H	H	Cl	Cl	H	Cl	Cl	CF_3	203.5-204.5
96	Cl	H	H	Cl	Cl	H	CF_3	H	CF_3	204-205
97	Cl	H	H	H	H	H	CF_3	H	CF_3	
98	Cl	H	H	H	H	H	Cl	H	CF_3	
99	Cl	H	H	H	Cl	H	H	Cl	H	
100	Cl	H	H	Cl	H	H	H	Cl		225-226.5
101	Cl	H	H	CF_3	H	H	H	Cl		198-199
102	Cl	H	H	CF_3	H	H	Cl	H	CF_3	183-185
103	Cl	H	H	Cl	Cl	H	H	Br		222-224
104	Cl	H	H	Cl	Cl	H	Br	Br	Br	232-233
105	Cl	H	H	Cl	Cl	H	CF_3	H	Cl	208-209

TABLE A (cont.)

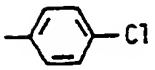
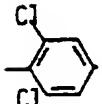
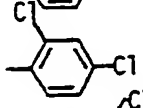
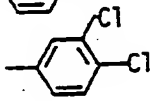
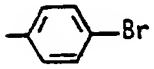
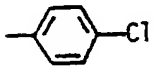
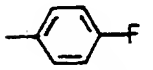
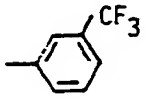
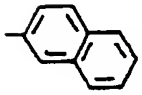
Cpd	X^1	X^2	X^3	X^4	X^5	X^6	R^1	R^2	R^3	m.p. (°C)
106	Cl	H	H	Cl	Cl	H	Cl	Cl	Cl	222-224
107	Cl	H	H	CH_3	CH_3	H	H	Cl		216-218
108	Cl	H	H	Cl	H	H	H	Br	H	243-245
109	Cl	H	H	CF_3	H	H	H	Br	H	184-186
110	Cl	H	H	Cl	Cl	H	H	H		184-187
111	Cl	H	H	Cl	Cl	H	H	H		211-213
112	Cl	H	H	Cl	Cl	H	H	H		220-221
113	Cl	H	H	Cl	Cl	H	H	H		210-211
114	Cl	H	H	CH_3	Cl	H	H	Cl		240-242
115	Cl	H	H	Cl	Cl	H	H	H		191-192
116	Cl	H	H	Cl	Cl	H	H	H		150-151
117	Cl	H	H	Cl	Cl	H	H	H		220-222
118	Cl	H	H	Cl	Cl	H	H	H		228-229
119	Cl	H	H	H	Cl	H	Cl	H	CF_3	209-210

TABLE A (cont.)

Cpd	X^1	X^2	X^3	X^4	X^5	X^6	R^1	R^2	R^3	m.p. (°C)
149	Cl	H	H	Cl	Cl	H	4-Br-phenyl	H	H	218-220
150	Cl	H	H	Cl	Cl	H	" "	Cl	H	225-229
151	F	F	H	Cl	Cl	H	" "	H	H	237-238
152	F	F	H	Cl	Cl	H	" "	Cl	H	301-305
153	F	F	H	Cl	Cl	H	H	H	4-CH_3-C_6H_4	198-202
154	Cl	H	H	Cl	Cl	H	H	H	4-CH_3-C_6H_4	205-210
155	H	H	H	Cl	Cl	H	H	H	4-Br-C_6H_4	256-259

TABLE B

Compounds of formula (A) wherein X^3 and X^6 are H, Y is O and $R^1 + R^2$ is $CH=CW^1-CW^2=CW^3$ (with W^3 in ortho-position of B)

Cpd	X^1	X^2	X^4	X^5	A	B	W^1	W^2	W^3	m.p. (°C)
23	F	F	Cl	Cl	N	CH	H	H	H	
24	F	F	Cl	Cl	N	C-Cl	H	H	H	235-237
25	F	F	Cl	Cl	N	C-Cl	H	H	Cl	
26	F	F	Cl	Cl	CH	N	Cl	Cl	H	225-228
27	F	F	Cl	H	CH	N	Cl	Cl	H	
28	F	F	Cl	Cl	N	N	H	Cl	H	(*)
29	F	F	Cl	Cl	N	N	Cl	Cl	H	242-244
120	Cl	H	Cl	Cl	N	CH	H	H	H	
121	Cl	H	Cl	Cl	N	C-Cl	H	H	H	
122	Cl	H	Cl	Cl	N	C-Cl	H	H	Cl	
123	Cl	H	Cl	Cl	CH	N	Cl	Cl	H	246-249
124	Cl	H	Cl	H	CH	N	Cl	Cl	H	225-228
125	Cl	H	Cl	Cl	N	N	H	Cl	H	103-106
126	Cl	H	Cl	Cl	N	N	Cl	Cl	H	222-225
127	F	F	H	Cl	C-CF_3	N	Cl	Cl	H	218-223

(*) isomer A : m.p. 196-198°
isomer B : m.p. 177-181°

128. N-3,5-dichloro-4-(2-indazolyl)phenyl-N'-2,6-difluorobenzoyl urea, m.p. 209-210°;

129. N-3,5-dichloro-4-(2-indazolyl)phenyl-N'-2-chlorobenzoyl urea, m.p. 216-217°;

130. N-3,5-dichloro-4-(4,5,6,7-tetrahydroisoindol-2-yl)phenyl-N'-2,6-difluorobenzoylurea, m.p. 240-242°;

131. N-3,5-dichloro-4-(2,5-dichloro-1-pyrrolyl)phenyl-N'-2,6-difluorobenzoylurea, m.p. 206-208°;

132. N-3,5-dichloro-4-(2,3,4,5-tetrachloro-1-pyrrolyl)phenyl-N'-2,6-difluorobenzoylurea, m.p. 244-245°;

133. N-3,5-dichloro-4-(3,4-dichloro-1-pyrrolyl)phenyl-N'-2,6-difluorobenzoylurea, m.p. 236-239°;

134. N-3,5-dichloro-4-[3-chloro-4-(2,4-dichlorophenyl)-1-pyrrolyl]phenyl-N'-2,6-difluorobenzoylurea, m.p. 200-206°;

135. N-3,5-dichloro-4-(4,5,6,7-tetrahydroisoindol-2-yl)phenyl-N'-2-chlorobenzoylurea, m.p. 230-231°;

136. N-3,5-dichloro-4-(2,5-dichloro-1-pyrrolyl)phenyl-N'-2-chlorobenzoylurea;

137. N-3,5-dichloro-4-(2,3,4,5-tetrachloro-1-pyrrolyl)phenyl-N'-2-chlorobenzoylurea, m.p. 234-235°;

138. N-3,5-dichloro-4-(3,4-dichloro-1-pyrrolyl)phenyl-N'-2-chlorobenzoylurea, m.p. 220-221°;

139. N-3,5-dichloro-4-[3-chloro-4-(2,4-dichlorophenyl)-1-pyrrolyl]phenyl-N'-2-chlorobenzoylurea, m.p. 177-181°;

140. N-3,5-dichloro-4-(4,5,6,6-tetrahydroisoindol-2-yl)phenyl-N'-2-chloro-5-fluorobenzoylurea;

141. N-3,5-dichloro-4-[3,4-bis(trifluoromethyl)-1-pyrazolyl]phenyl-N'-2-chloro-5-fluorobenzoylurea;

142. N-3,5-dichloro-4-(4,5-dichloro-1-benzotriazolyl)phenyl-N'-2-chloro-5-fluorobenzoylurea;

143. N-3,5-dichloro-4-(4,5,6,7-tetrahydroisoindol-2-yl)phenyl-N'-2-chlorobenzoylthiourea;

144. N-3,5-dichloro-4-(3,4-dichloro-1-pyrrolyl)phenyl-N'-2-chlorobenzoylthiourea;

145. N-3,5-dichloro-4-[3,4-bis(trifluoromethyl)-1-pyrazolyl]phenyl-N'-2-chlorobenzoylthiourea;

146. N-3,5-dichloro-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]phenyl-N'-2-chlorobenzoylthiourea;

147. N-3,5-dichloro-4-(4,5-dichloro-1-benzotriazolyl)phenyl-N'-2-chlorobenzoylthiourea;

148. N-3,5-dichloro-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]phenyl-N'-2,6-difluorobenzoylurea, m.p. 166-167.5°.

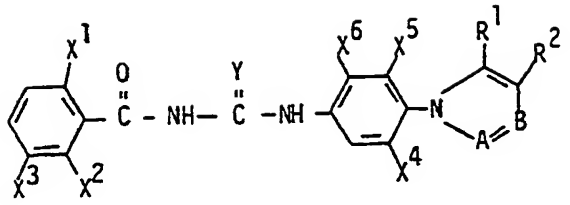
BIOLOGICAL ACTIVITY

Example 4

Early (0-24 hr) third instar larvae of the tobacco budworm, Heliothis virescens, are topically treated on the dorsal abdomen with 1 microlitre of acetone dilution of the test compound at the concentration to be tested. The treated larvae are placed on artificial diet in individual cells of a plastic grid contained in a covered plastic petri dish. The containers are held at 27°C, 16 hour photoperiod until all larvae are either dead or have molted to fifth instar larvae. In general, insecticidal activity is observed after application of from about 0.004 to 0.070 microgram test compound (4 to 70 ppm) per insect.

CLAIMS

1. Compounds of formula (A)



(A)

wherein, each of X^1, X^2, X^3 and X^5 is independently hydrogen, halogen or C_{1-4}alkyl;

X^4 is hydrogen, halogen, unsubstituted or halogenated C_{1-4}alkyl or COOR;

X^6 is hydrogen, halogen, C_{1-8}alkyl or COOR';

Y is oxygen or sulfur;

A is nitrogen or C-R^4;

B is nitrogen or C-R^3;

each of R^1 and R^4 is independently hydrogen, halogen, halogenated C_{1-8}-alkyl, unsubstituted or halogenated C_{1-8}alkoxy, unsubstituted or halogenated C_{1-8}alkylthio or; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogen atoms or with a CF_3, C_{1-4}alkyl or C_{1-4}alkoxy group and 0 to 3 halogen atoms;

each of R^2 and R^3 is independently hydrogen; halogen; cyano; unsubstituted or halogenated C_{1-8}alkyl; unsubstituted or halogenated C_{1-8}-alkoxy; unsubstituted or halogenated C_{1-8}alkylthio; COOR"; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogenatoms or with a C_{1-4}alkyl, C_{1-4}alkoxy or CF_3 group and 0 to 3 halogen atoms; or either R^1 and R^2 or R^2 or R^3 can together form a bridging group of 4 carbon atoms, saturated or unsaturated, and optionally substituted with 1 to 4 halogen atoms or with a trifluoromethyl group and 0 to 3 halogen atoms;

each of R, R' and R" is hydrogen or C_{1-8}alkyl;

with the proviso that where A is C-R^4 and B is C-R^3, not all of R^1, R^2, R^3 and R^4 may be hydrogen.

2. A compound according to Claim 1 wherein A is nitrogen and B is C-R^3.

3. A compound according to Claims 1 or 2 wherein any aryl, aryloxy or arylthio is unsubstituted or mono- or disubstituted with one methyl, methoxy or CF_3 group and zero or one halogen or with one or two halogen, and whereby aryl - as such or in the terms aryloxy and arythio - refers to naphthyl, phenyl, pyridyl or thienyl.

4. A compound according to Claim 3, wherein Y is O.

5. A compound according to Claim 3 or 4, wherein

each of X^1, X^2 and X^3 is independently H or halogen,

X^4 is H, halogen, CH_3 or CF_3,

X^5 is H, halogen or CH_3,

X^6 is H or halogen,

each of R^1 and R^2 is independently H, halogen or CF_3,

R^3 is H, halogen, C_{1-4}alkyl or CF_3 whereby one of R^1, R^2 and R^3 may also be halophenyl, dihalophenyl, methylphenyl or trifluoromethylphenyl and/or

R^1 and R^2 together may form a bridging group of the formula CH=C-CH=CH, which group is unsubstituted or mono- or dihalogenated, or

R^2 and R^3 together form a bridging group of formula $(CH_2)_4$.

6. A compound according to Claim 5, wherein X^1 is halogen, X^3 and X^6 are H, X^4 is halogen or CH_3 and R^3 is H, halogen, CF_3 or halophenyl.

7. A compound according to Claim 6 selected from

a) N-3,5-dichloro-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]-phenyl-N'-2,6-difluorobenzoylurea,

b) N-3,5-dimethyl-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]-phenyl-N'-2,6-difluorobenzoylurea,

c) N-3,5-dichloro-4-(4-bromo-1-pyrazolyl)-phenyl-N'-2-chlorobenzoylurea,

d) N-3,5-dichloro-4-(3,4-dibromo-1-pyrazolyl)phenyl-N'-2-chlorobenzoylurea,

e) N-3,5-dichloro-4-(4,5-dichloro-3-trifluoromethyl-1-pyrazolyl)phenyl-N'-2-chlorobenzoylurea,

f) N-3,5-dichloro-4-[3-(4-chlorophenyl)-1-pyrazolyl]-phenyl-N'-2-chlorobenzoylurea,

g) N-3,5-dichloro-4-(3,4,5-trichloro-1-pyrazolyl)phenyl-N'-2-chlorobenzoylurea,

h) N-3,5-dichloro-4-(4,5-dichloro-3-trifluoromethyl-1-pyrazolyl)phenyl-N'-2-fluorobenzoylurea,

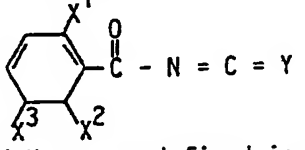
i) N-3,5-dichloro-4-[3-(4-bromophenyl)-1-pyrazolyl]-phenyl-N'-2-fluorobenzoylurea.

8. A pesticidal composition comprising a compound as defined in any one of Claims 1 to 7 and an agriculturally acceptable diluent.

9. A method of combatting pests which comprises applying to the pest or its locus a pest-controlling amount of a compound of formula (A) as defined in any one of Claims 1 to 7.

10. A process for preparing a compound of Claims 1 to 7 which comprises

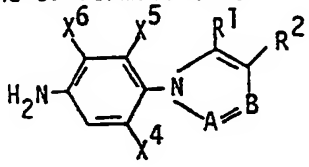
a) reacting a compound of formula (I)



(I)

wherein X^1, X^2, X^3 and Y are as defined in Claim 1,

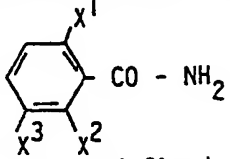
with a compound of formula (II)



(II)

wherein X^4, X^5, X^6, R^1, R^2, A and B are as defined in Claim 1,

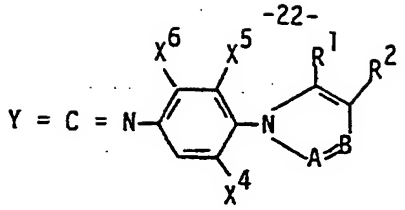
or by b) by reacting a benzamide of formula (III)



(III)

wherein X^1, X^2 and X^3 are as defined in Claim 1,

with a compound of formula (IV)



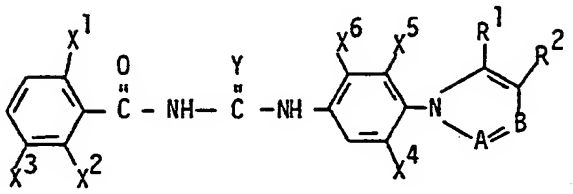
(IV)

wherein Y, R^1, R^2, X^4, X^5, X^6, A and B are as defined in Claim 1.

AT-ES-GR

CLAIMS

1. A pesticidal composition comprising a compound of formula (A)



(A)

wherein, each of X^1, X^2, X^3 and X^5 is independently hydrogen, halogen or C_{1-4}alkyl;
X^4 is hydrogen, halogen, unsubstituted or halogenated C_{1-4}alkyl or COOR;
X^6 is hydrogen, halogen, C_{1-8}alkyl or COOR';
Y is oxygen or sulfur;
A is nitrogen or C-R^4;
B is nitrogen or C-R^3;
each of R^1 and R^4 is independently hydrogen, halogen, halogenated C_{1-8}-alkyl, unsubstituted or halogenated C_{1-8}alkoxy, unsubstituted or halogenated C_{1-8}alkylthio or; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogen atoms or with a CF_3, C_{1-4}alkyl or C_{1-4}alkoxy group and 0 to 3 halogen atoms;
each of R^2 and R^3 is independently hydrogen; halogen; cyano; unsubstituted or halogenated C_{1-8}alkyl; unsubstituted or halogenated C_{1-8}-alkoxy; unsubstituted or halogenated C_{1-8}alkylthio; COOR"; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogenatoms or with a C_{1-4}alkyl, C_{1-4}alkoxy or CF_3 group and 0 to 3 halogen atoms; or either R^1 and R^2 or R^2 or R^3 can together form a bridging group of 4 carbon atoms, saturated or unsaturated, and optionally substituted with 1 to 4 halogen atoms or with a trifluoromethyl group and 0 to 3 halogen atoms;
each of R, R' and R" is hydrogen or C_{1-8}alkyl;
with the proviso that where A is C-R^4 and B is C-R^3, not all of R^1, R^2, R^3 and R^4 may be hydrogen, and an agriculturally acceptable diluent.

2. A composition according to Claim 1 wherein A is nitrogen and B is C-R^3.

3. A composition according to Claims 1 or 2 wherein any aryl, aryloxy or arylthio is unsubstituted or mono- or disubstituted with one methyl, methoxy or CF_3 group and zero or one halogen or with one or two halogen, and whereby aryl - as such or in the terms aryloxy and arythio - refers to naphthyl, phenyl, pyridyl or thienyl.

4. A composition according to Claim 3, wherein Y is O.

5. A composition according to Claim 3 or 4, wherein

each of X^1, X^2 and X^3 is independently H or halogen,

X^4 is H, halogen, CH_3 or CF_3,

X^5 is H, halogen or CH_3,

X^6 is H or halogen,

each of R^1 and R^2 is independently H, halogen or CF_3,

R^3 is H, halogen, C_{1-4}alkyl or CF_3 whereby one of R^1, R^2 and R^3 may also be halophenyl, dihalophenyl, methylphenyl or trifluoromethylphenyl and/or

R^1 and R^2 together may form a bridging group of the formula CH=C-CH=CH, which group is unsubstituted or mono- or dihalogenated, or

R^2 and R^3 together form a bridging group of formula $(CH_2)_4$.

6. A composition according to Claim 5, wherein X^1 is halogen.

7. A composition according to Claim 6,

wherein X^3 and X^6 are H,

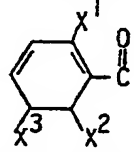
X^4 is halogen, CH_3 or CF_3,

X^5 is halogen or CH_3

and R^3 is H, halogen, CF_3 or halophenyl.

8. A process for preparing a compound of Claims 1 to 7 which comprises

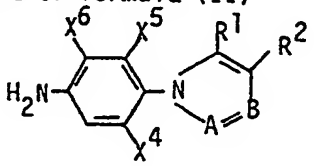
a) reacting a compound of formula (I)



(I)

wherein X^1, X^2, X^3 and Y are as defined in Claim 1,

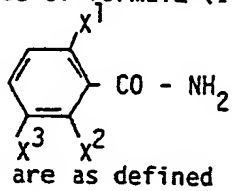
with a compound of formula (II)



(II)

wherein X^4, X^5, X^6, R^1, R^2, A and B are as defined in Claim 1,

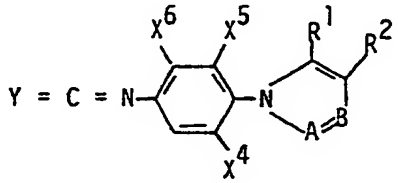
or by b) by reacting a benzamide of formula (III)



(III)

wherein X^1, X^2 and X^3 are as defined in Claim 1,

with a compound of formula (IV)



(IV)

wherein Y, R^1, R^2, X^4, X^5, X^6, A and B are as defined in Claim 1.